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Abstract
The review of ferroelectric properties at the nanoscale is presented. Determining the nanoscale, authors bear in mind the film thickness equal by the order of value to the size of critical domain nucleus. Three phenomena are considered: ferroelectric switching, scaling of coercive field and bulk photovoltaic effect. The investigation of ferroelectricity at the nanoscale started 20 years ago. The nanoscaled ferroelectricics with perovskite structure came to be considered only the last few years.

Keywords Ferroelectricity; Nanoscale

Some historical remarks

In 1945-46 the ferroelectric properties of $BaTiO_3$ were discovered by Vul (in Russia)[1] and by von Hippel (in USA)[2]. It stimulated the development of the mean field theory of ferroelectricity by Ginzburg (so called Landau – Ginzburg – Devonshire (LGD) theory)[3,4].

In LGD theory the switching take place at $E > E_c$, where E_c is the coercive field. We shall call this LGD value of E intrinsic coercive field. Thus LGD switching theory is supposed to be the intrinsic or homogeneous. Figure 1 taken from Ginzburg paper shows LGD dependence of free energy on polarization P for different external field E and illustrates intrinsic (homogeneous) switching. As seen from Figure 1, LGD switching is characterized by the threshold $E=E_{cin}$. At $E < E_{cin}$ there is no switching. LGD intrinsic switching has never been observed experimentally before 1998 in the bulk crystals and films and experimental values of coercive field E_{cex} were found by two-tree orders of value less then intrinsic coercive field $E_{cex} << E_{cin}$

This contradiction remained unsolved for few years until the discovery by Chernysheva and coauthors of domains in Rochell salt[5]. Later Merz observed domains in $BaTiO_3$ and showed, that the movement of domains in the external field causes the switching of the polarization[6]. The same conclusion for Rochell salt was made by Indenbom[7]. The theory of domain (extrinsic) switching

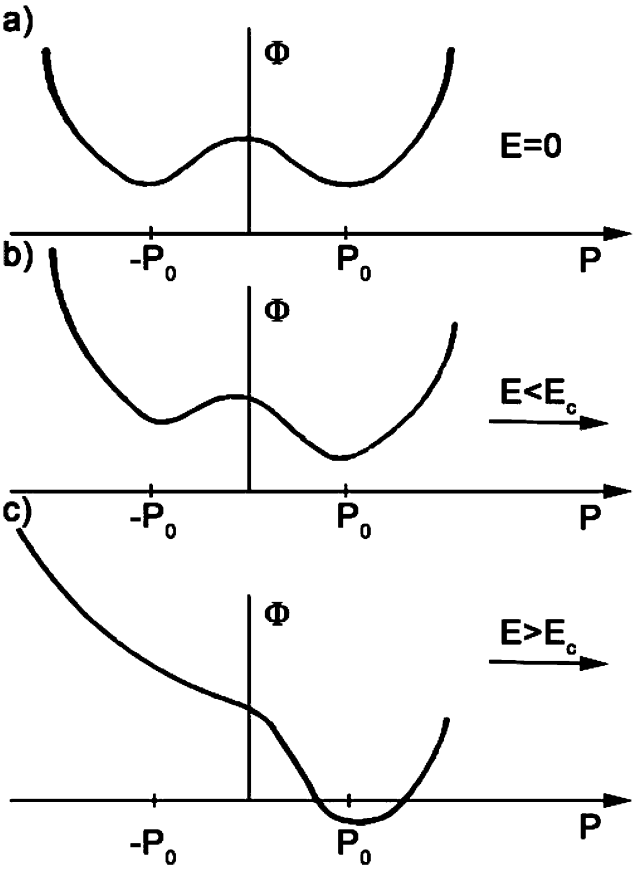

Figure 1. Switching in the LGD theory.

has been developed later by Ishibashi and Takagi at Kolmogorov approach (KAI)[8]. The full and comprehensive review of the extrinsic (domain) mechanism is given in Reference 9.

Thus the LGD mean field theory successfully explained the ferroelectric properties, including ferroelectric phase transitions of the second and first order (in vicinity of the second one), but could not explain switching and its peculiarities. This situation remained until discovery and investigation of nanosized polymeric Langmuir-Blodgett (LB) films[10,11]. One impressive possibility of the LB method is the opportunity to vary the thickness of LB films to an accuracy of monolayer (0,5 nm), when the kind of molecules as well as their orientation can be controlled by ellipsometry, tunnel and atomic force microscopy.

The nanosized ferroelectric films of copolymer vinylidene-fluoride trifluorethylene were grown and investigated in a series of papers[12-15]. The investigation and application of the thin ferroelectric films have long history[16], but LB method for the first time made possible to obtain and investigate the films with thickness equal by the order of value to the critical domain nucleus size. As well known, the size of critical domain nucleus supposed to be in the interval $l \approx 1$–10 nm[16-18]. Therefore at the nanoscale the ferroelectric films could reveal nucleation and only initial stage of domain growth. Nevertheless the LB ferroelectric copolymers have shown switching[11], which KAI theory could not explain.

Switching at the nanoscale

It was supposed in References 19 & 20 that the ferroelectric films at the nanoscale (1-10 nm) are switched by the intrinsic (homogenous) LGD mechanism. The kinetics of intrinsic switching is described by the Landau–Khalatnikov equation:

$$\xi \frac{dP}{dt} = -\alpha P - \beta P^3 - \gamma P^5 + E \tag{1}$$

where P is spontaneous polarization, α, β, and γ are well known Landau–Ginzburg coefficients for the first order ferroelectrics, E is external field, ξ is damping coefficient. Equation (1) describes the intrinsic switching kinetics in frame of homogenous mean field theory. The solution of (1) has the critical character [19]:

$$\tau^{-1} = \frac{1}{\tau_0}\left(\frac{E}{E_{cin}} - 1\right)^{1/2} \tag{2}$$

where τ is switching time, $\tau_0 \approx 6.3\gamma\xi/\beta^2$, E_{cin} is intrinsic coercive field, $E_{cin} \approx P/\varepsilon\varepsilon_0$. As seen from Equation (2), at $E < E_{cin}$ there is no switching. Switching takes place only at $E > E_{cin.}$

Thus intrinsic LGD switching, as was mentioned, has the threshold $E = E_{cin}$. On the contrary the domain-driven mechanism (KAI) does not show the threshold. In the simplest case KAI theory gives for the switching time the value[8]:

$$\tau^{-1} = \tau_0^{-1} exp\left(-\frac{E_0}{E}\right) \tag{3}$$

where τ_0 and E_0 are constants.

Intrinsic switching kinetics

For the first time the intrinsic LGD switching was found in the LB copolymer films with thickness 1 nm[11] and its kinetics, was investigated in many papers by condenser methods of Merz and Chinoweth[19,21,22] and by means of atomic force microscope in piezoelectric regime (PFM) [23,24].

Figures 2a and 2b show the dependence of reciprocal switching time on the external voltage V for LB copolymer. Figure 2a for thickness l = 15 nm reveal $E_{cin} \approx 10^9$ V/cm, what correlated with LGD value for vinylidene-fluoride trifluorethylene copolymer[20]. The solid curve corresponds to (2). The data obtained by Merz method—Figure 2b—shows the same dependences for the thickness l = 5, 15 and 50 nm. The thick copolymer film reveals KAI dependence (3). Two films at the nanoscale (5 and 15 nm) in spite of point scattering show threshold at V = 4v. The solid curves correpond (2) for l = 5, 15 nm and (3) for 50 nm. These data are obtained by Chinoweth method. The same results are obtained by PFM[23, 24].

The homogeneous LGD switching, obtained in References 19, 21-24, for the ferroelectric copolymer films at the nanoscale led many authors[9] to the conclusion that this polymer ferroelectric switching is possibly an exception. Ferroelectric perovskite films at the nanoscale were prepared only during last 10 years and homogeneous character of their switching has not been revealed. The comprehensive review on preparation of perovskite superlattices at the nanoscale is given in

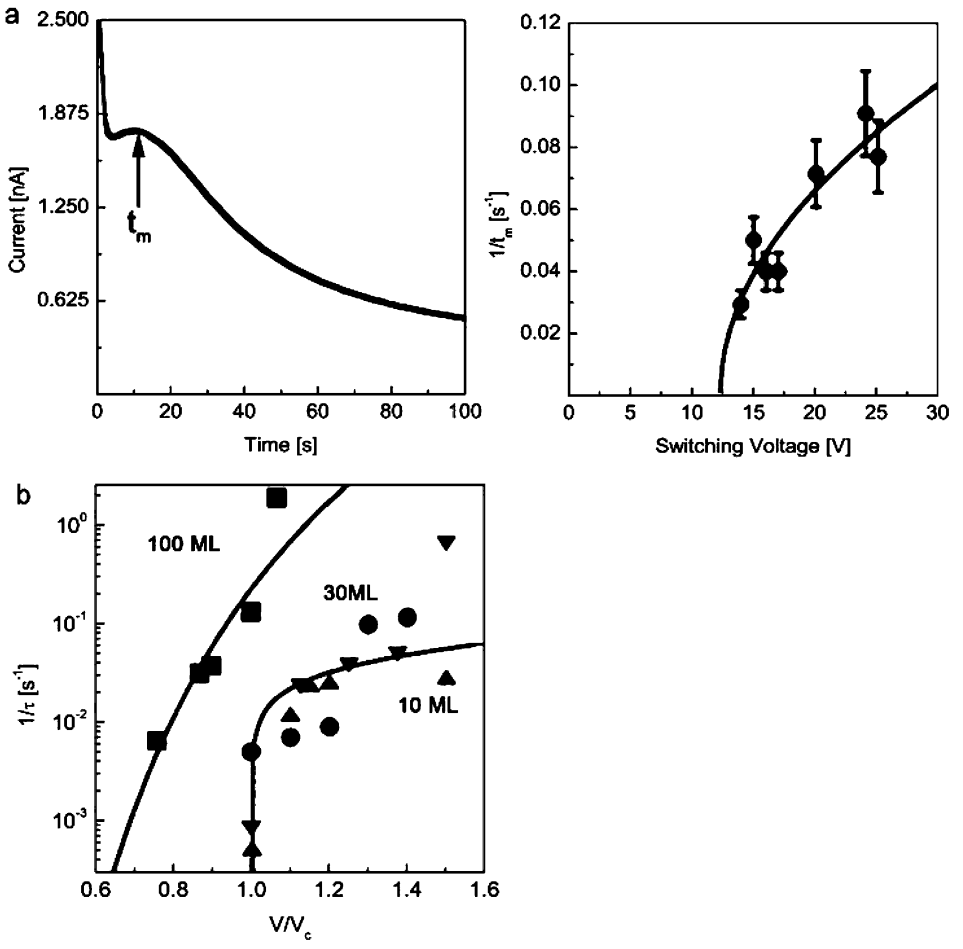

Figure 2. a,b Intrinsic and extrinsic switching in the ferroelectric copolymer.

Reference 25. The ferroelectricity is found for nanoscaled epitaxial perovskite films as thin as three elementary cells (1,2 nm) [26-29], but the intrinsic properties are not investigated. There is only one paper[30], where homogeneous switching in $PbTiO_3$ films at the nanoscale was supposed, but switching kinetics was not investigated.

In Reference 31 the switching kinetics for the ultrathin heteroepitaxial $BaTiO_3$ films was investigated in condenser, and for the first time homogeneous intrinsic switching was revealed. It was shown also, that the measured coercive field coincides well with the value obtained from LGD phenomenology.

Barium titanate (BTO) ultrathin films were grown by pulsed laser deposition (PLD) onto Pt-MgO (100) substrates in a single vacuum cycle[18,19]. The structural properties of the composite system (including the thickness of BTO films) are investigated by Rutherford backscattering spectrometry channeling and cross-sectional transmission electron microscopy. The heteroepitaxial growth of $BaTiO_3$ on top of Pt is illustrated by the high resolution transmission electron microscopy of the sample cross-section with fast Fourier transform taken at both MgO/Pt and Pt/$BaTiO_3$ interfaces (Figure 3). The thickness of $BaTiO_3$ films 2, 8, and 40 nm has been measured by

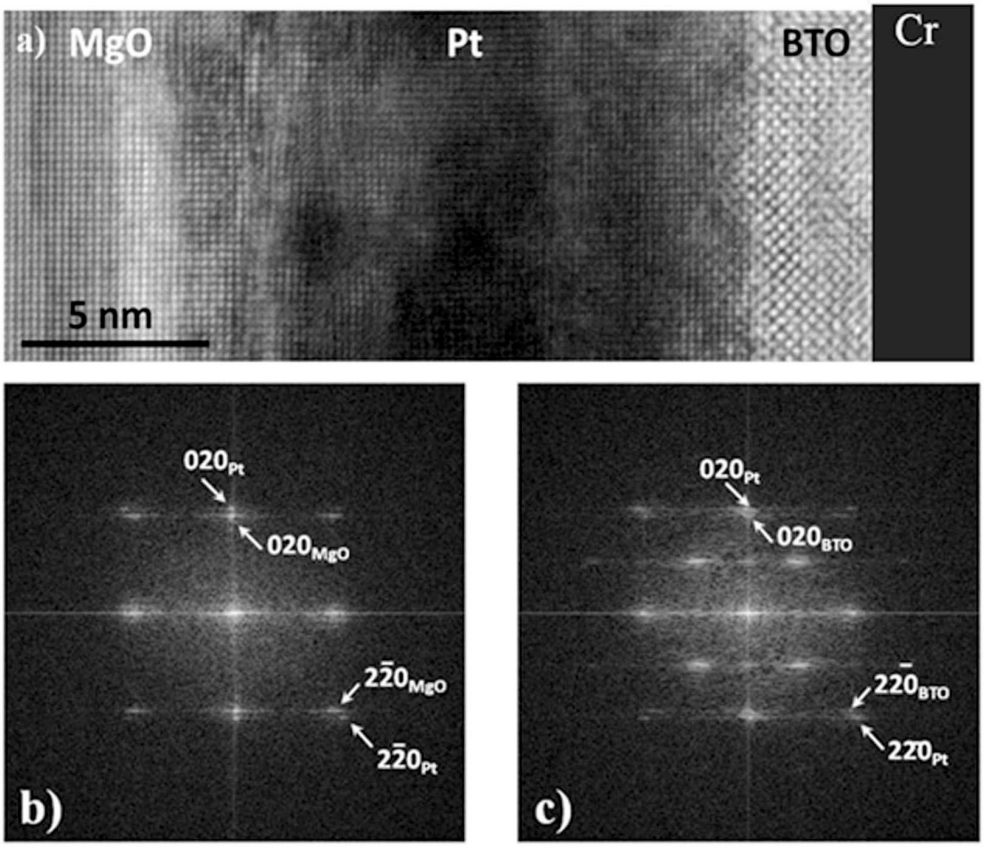

Figure 3. The MgO/Pt/BTO epitaxial thin film (a).Electron diffraction patterns from the Pt/MgO interface (b) and the Pt/BTO interface (c).

Rutherford backscattering spectrometry (RBS) with 2 MeV He^{++} ions with accuracy 10%[32]. For the condenser measurements the second electrode Au was grown on surface of barium titanate film in UVH (Figure 4). The electrode measurements were performed by means of PFM, which tip contacted Au electrode. The electrodes were deposited by lithography and had a form of circles with radius of a few microns.

The hysteresis loops and kinetics measurements were investigated in two regimes. In the first regime the tip contacted with the barium titanate film surface and external voltage was applied

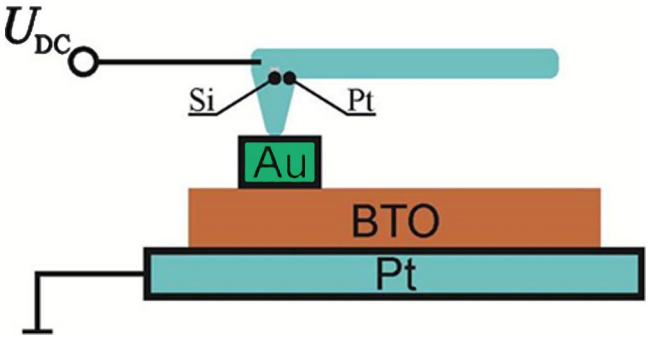

Figure 4. Measurements in condenser by means of PFM.

between tip and Pt substrate. In the second regime the measurements were performed in condenser and external voltage was applied between Pt and Au electrode. In this case the upper Au electrode (20 nm) was evaporated in UHV on the barium titanate surface (Figure 4).

All films in the scale 3–40 nm show homogeneous stable monodomain state.

The distinction between the intrinsic and extrinsic behavior is well illustrated by Figure 5 which shows switching rate as a function of the bias voltage for the ultrathin epitaxial $BaTiO_3$ film 8 nm thick (Figure 5a,b) and for $BaTiO_3$ single crystal 1 mm thick in [001] axis (Figure 5c). Figure 6a shows the dependence τ^{-2} as function of V for $BaTiO_3$ film in condenser. Figure 5b shows the same dependence for the tip in contact with free surface of the film (tip regime). The experimental data are satisfactory fitted with Equation (1), showing that coercive field $E_c = E_{cin}$. Both regimes show the same intrinsic behavior in spite of small difference in values of switching time and E_{cin} is close to the LGD value $P/\varepsilon\varepsilon_0 \approx 10^8$ v/m.

On the contrary, the switching kinetics for the single crystal (Figure 5c) agrees with Equation (3) and switching occurs at $V = V_{cex} << V_{cin.}$

The results of the switching measurements confirm the existence of intrinsic homogeneous switching in the ultrathin ferroelectric films, which thickness is equal by the order of value to the size of domain critical nucleus. At transition from crystals and thick ferroelectric films to the ultrathin films, the KAI mechanism is replaced by the homogeneous one. In reality, in this thickness range, the competition between homogeneous and domain driven mechanisms takes place, which depends on thickness and external field. It recently was confirmed by "ab initio" approach[34]. This is because the rate of extrinsic switching depends exponentially on the applied field, Equation (3), while the rate of intrinsic switching increases only as the square root of the field, Equation (2). The extrinsic nature of the high-field regime was well illustrated by the recent work of Chanthbouala et al[35]. We suppose that this two-mechanisms competition is a common phenomenon for all ferroelectric materials, and the thickness transition criterion is the size of the critical domain nucleus.

LGD phenomenology and experiment do not reveal the microscopic picture. Preliminary remarks were done in Reference 30, in accordance with which, we can suggest the following microscopic picture (see Figure 6).

At the nanoscale there is a competing of extrinsic (domain-driven, KAI) and intrinsic (LGD) mechanisms. For the thickness of the ferroelectric film comparable with critical domain size (1–10 nm)[16-18] (see also Miller-Weinreich value of 5 nm) the intrinsic mechanism prevails. Because experiment shows the homogeneous polarization in such films, the switching could be supposed homogeneous and described by LGD phenomenology.

The scaling of coercive field

All ferroelectric films show dependence of coercive field on the thickness $E_{cex} = E_{cex}(l)$. The intrinsic LGD coercive field E_{cin} does not depend on thickness and determined by Landau-Ginzburg coefficients[20].

Figure 7a shows the scaling $E_c = E_c(l)$ for the ferroelectric vinylidene fluoride copolymer P[VDF-TrFE] films, obtained by Langmuir-Blodgett (LB) method [20]. The LB films thinner than 10 nm show $E_c = E_{cin} \approx 10^9$ V/m, which does not depend on the film thickness l and coincides by the order of value with the LGD intrinsic coercive field. Thicker LB films (circle symbols) and thick films, obtained by spun method (diamond symbols), show scaling. Therefore in Reference 20 it has been supposed that films in the interval 1–10 nm reveal LGD intrinsic (homogeneous) switching kinetics (1,2), which were observed later[19, 21-24]. On the contrary at $l > 10$ nm the copolymer ferroelectric films could reveal switching, governed by domain dynamics (KAI mechanism)[8].

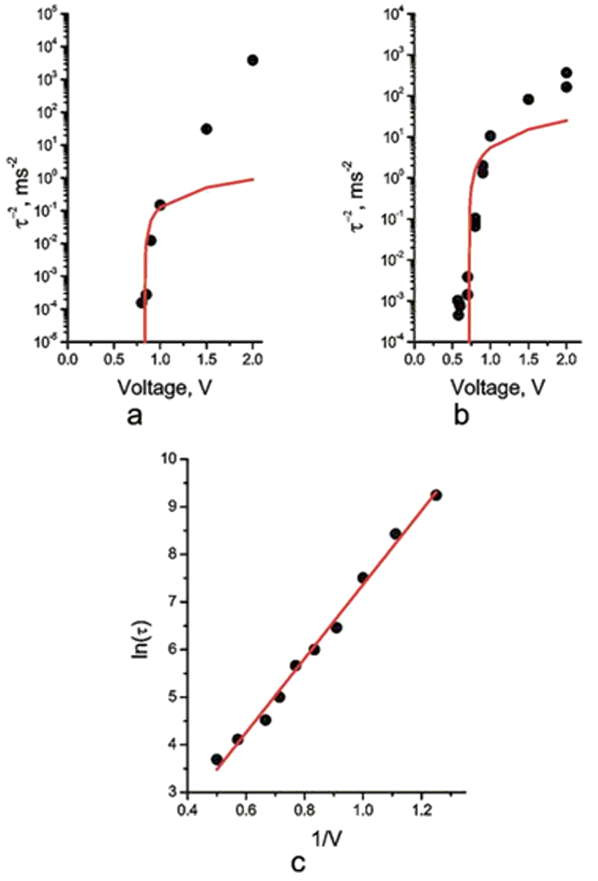

Figure 5. Intrinsic and extrinsic switching in BTO film at the nanoscale.

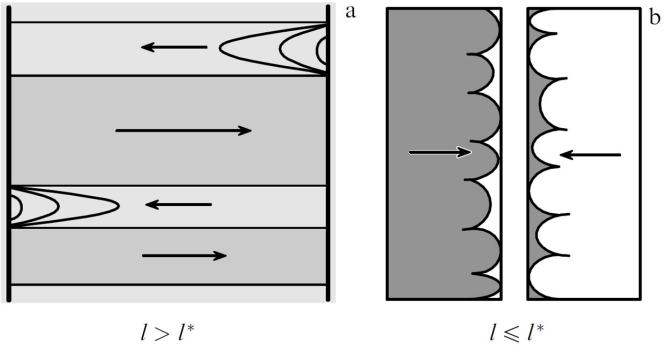

Figure 6. The scheme of domain driving (left side) and intrinsic (homogeneous) switching.

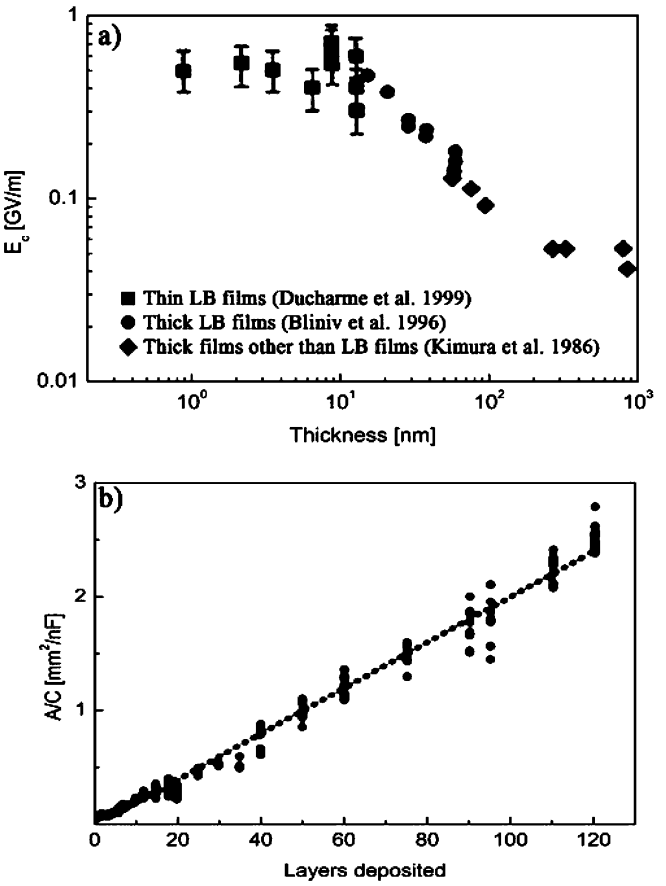

Figure 7. Scaling of coercive field in the ferroelectric copolymer (a). Condenser capacity as a function of copolymer thickness (b).

The results shown on Figure 7a were obtained in condenser Al- P[VDF-TrFE]-Al by the Sawyer-Tower method.

The authors of Reference 36 supposed that the saturation on the curve of Figure 6a is caused by the Thomas-Fermi gap between Al electrodes and copolymer film. But the dependence of condenser capacity on the number of LB monolayers (or on the film thickness) did not reveal any gap (Figure 7b)[37].

Here we show the same type of scaling for the laser-epitaxial $BaTiO_3$ ultrathin films with $l < 10$ nm[38]. The measurements were performed in condenser Pt-$BaTiO_3$-Au by means of PFM, which tip contacted one of the electrodes (Figure 4). The electrodes on the surface of $BaTiO_3$ were deposited by lithography and had the form of circles with radius of a few microns. Figure 8 shows hysteresis loops obtained for film thicknesses of 3, 8, and 40 nm. Figure 8 also shows the scaling of $E_c = E_c(l)$ in the region 3–40 nm. Scaling takes place at $l > 10$ nm, but at $l < 10$ nm the coercive field weakly depends on l and its value is near $E_{cin} \approx 10^8$ V/m, which coincides with the LGD value. Correspondingly the films with $l = 3$ and 8 nm reveal homogeneous LGD switching kinetics (1,2) and thicker films – KAI behavior (3).

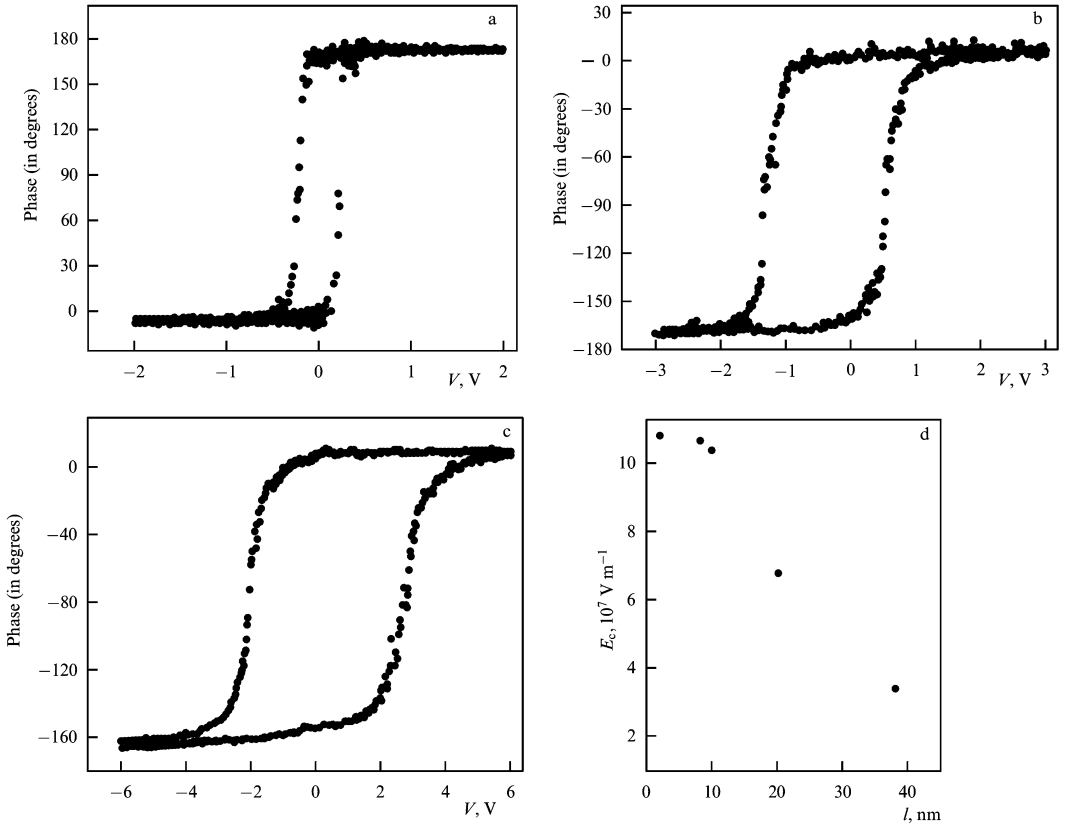

Figure 8. Scaling of coercive field in the BTO film

Photovoltaics in the ferroelectrics at the nanoscale

Here we make preliminary and short comments about photovoltaics.

The monodomain ferroelectric films at the nanoscale could be used for the Bulk Photovoltaic Effect (BPE) and transformation of light energy into electric one with very high efficiency η.

The BPE was discovered at the late 1960s[39]. BPE arises under illumination of the homogeneous crystal without center of symmetry and is caused by the violation of the Boltzman principle of detailed balancing.

In the bulk ferroelectric crystals and films the efficiency η is very small in spite of high voltages $V >> E_g$, which could be generated at open circuit conditions (E_g is energy gap).

$$\eta = \frac{\tau_{nth}}{\tau_{th}} = 10^{-6} \div 10^{-4} \tag{4}$$

where τ_{nth} is the lifetime of the nonthermalized (hot) carriers, τ_{th} is the lifetime of thermolized carriers. But at the nanoscale η could be large if we suppose the large quantum yield. For monodomain 2–3 nm $BaTiO_3$ films, $\tau_{nth} = \tau_{th}$ because the shift of hot carriers is equal by the order of value

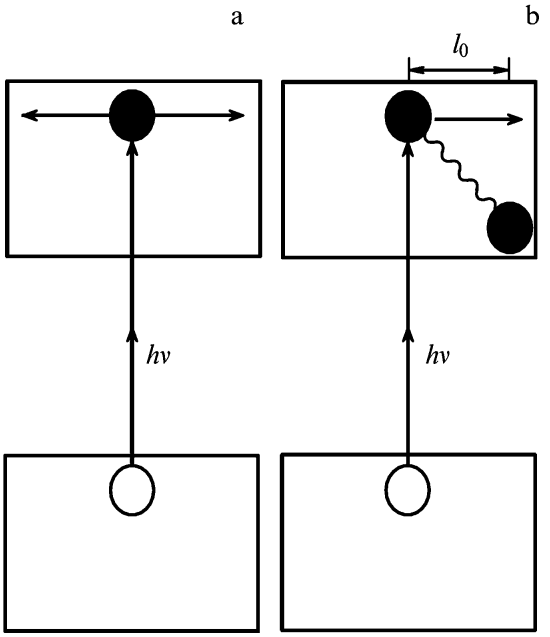

Figure 9. Symmetric distribution of nonequilibrium carriers in a symmetric crystal (left); asymmetric distribution of nonthermolized carriers in a noncentrosymmetric crystal (right).

to the distance between electrodes. Figure 9 shows the absence of BPE in the centrosymmetric crystals (left part) and appearance of BPE in ferro- and piezoelectric crystals.

The experiments on photovoltaics in the $BaTiO_3$ films at the nanoscale are in progress.

Conclusions

The ferroelectric properties at the nanoscale could not be explained simply by the finite size effect. They are caused by competing (coexistence) of intrinsic and extrinsic behavior, which depends on the thickness and external field. At the ferroelectric film thickness $l > l^*$ prevails extrinsic coercive field and switching. At $l < l^*$ ferroelectric film reveals intrinsic homogeneous switching and coercive field, predicted by LGD phenomenology.

LGD phenomenology for ferroelectricity (1946) was developed for the homogeneous space and could not explain the switching properties. KAI theory, developed for domain-nonhomogeneous space (1970), explained the experimental value of coercive field and switching kinetics in crystal and films. The ultrathin films—with thickness equal by the order of value to domain critical size—could be considered as homogeneous. For these films LGD phenomenology explained all the ferroelectric properties, including the switching (1993-2013).

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